Uranium oxide interference correction algorithms

Measurement of the uranium isotopic composition of double-spiked \(^{233}\text{U}-^{235}\text{U}\) samples as \(\text{UO}_2^+\) species requires the subtraction of the isobaric interference of \(^{18}\text{O}\)-bearing \(^{233}\text{UO}_2\) on the predominant target \(^{235}\text{U}\text{O}_2\) peak at mass 267. The probability of forming a double \(^{17}\text{O}\)-bearing uranium dioxide molecule is so low as to make a \(^{233}\text{U}^{17}\text{O}_2\) interference of negligible importance for this measurement. The probability of an \(^{18}\text{O}\) dioxide substitution is estimated by the relative abundance of \(^{18}\text{O}\), also safely approximated by \(^{18}\text{O}/^{16}\text{O}\), which is assigned a value of 0.002 (IUPAC, 1997). Both possible \(^{18}\text{O}\) substitutions into the dioxide molecule must be considered. The maths for the correction of the two measured U isotope ratios are given below.

For correcting the \(^{235}\text{U}/^{233}\text{U}\) (or \(^{233}\text{U}/^{235}\text{U}\)) ratio:

\[
\left(\frac{267}{265}\right)_{\text{meas}} = \frac{^{235}\text{U}^{16}\text{O}^{16}\text{O} + ^{233}\text{U}^{16}\text{O}^{16}\text{O} + ^{233}\text{U}^{16}\text{O}^{18}\text{O}}{^{233}\text{U}^{16}\text{O}^{16}\text{O}} \tag{1}
\]

\[
^{233}\text{U}^{18}\text{O}^{16}\text{O} = ^{233}\text{U}^{16}\text{O}^{18}\text{O} = ^{233}\text{U}^{16}\text{O}^{16}\text{O} \frac{^{18}\text{O}}{^{16}\text{O}} \tag{2}
\]

\[
\left(\frac{267}{265}\right)_{\text{meas}} = \frac{^{235}\text{U}^{16}\text{O}^{16}\text{O} + ^{233}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right) + ^{233}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)}{^{233}\text{U}^{16}\text{O}^{16}\text{O}} \tag{3}
\]

\[
\left(\frac{267}{265}\right) = \frac{^{235}\text{U}^{16}\text{O}^{16}\text{O} + ^{233}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right) + ^{233}\text{U}^{16}\text{O}^{16}\text{O} \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)}{^{233}\text{U}^{16}\text{O}^{16}\text{O}} \tag{4}
\]

\[
\left(\frac{267}{265}\right)_{\text{meas}} = \left(\frac{267}{265}\right)_{\text{true}} + \left[\frac{^{18}\text{O}}{^{16}\text{O}}\right] + \left[\frac{^{18}\text{O}}{^{16}\text{O}}\right] \tag{5}
\]

\[
\frac{^{235}\text{U}^{16}\text{O}^{16}\text{O}}{^{233}\text{U}^{16}\text{O}^{16}\text{O}} = \left(\frac{267}{265}\right)_{\text{true}} \tag{6}
\]

\[
\left(\frac{267}{265}\right)_{\text{meas}} = \left(\frac{267}{265}\right)_{\text{true}} + \left[\frac{^{18}\text{O}}{^{16}\text{O}}\right] + \left[\frac{^{18}\text{O}}{^{16}\text{O}}\right] \tag{7}
\]

\[
\left[\frac{^{18}\text{O}}{^{16}\text{O}}\right] = 0.002 \quad \text{(IUPAC 1997)} \tag{8}
\]
The final form of eqn. 11 accommodates those accustomed to both measuring and then entering the $^{233}\text{U} /^{235}\text{U}$ ratio into data reduction software.

For correcting the $^{238}\text{U} /^{235}\text{U}$ ratio:

\[
\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{true}} = \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{meas}} \times \left( \frac{^{265}\text{U}}{^{267}\text{U}} \right)_{\text{true}}
\] (12)

\[
\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{true}} = \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{meas}} \times \left( \frac{^{265}\text{U}}{^{267}\text{U}} \right)_{\text{true}}
\] (13)

Combining with eqn. 11…

\[
\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{true}} = \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{meas}} \times \frac{1}{\left( \frac{^{265}\text{U}}{^{267}\text{U}} \right)_{\text{true}}} - 0.004
\] (14)

For those used to measuring the $^{238}\text{U} /^{235}\text{U}$ and $^{233}\text{U} /^{235}\text{U}$ ratios…

\[
\left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{true}} = \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{meas}} \times \frac{1}{\left( \frac{^{265}\text{U}}{^{267}\text{U}} \right)_{\text{meas}}} - 0.004
\] (15)
This last form accommodates those accustomed to both measuring and entering the
$^{238}\text{U}/^{235}\text{U}$ and $^{233}\text{U}/^{235}\text{U}$ ratios into data reduction software. For Sector-54 users measuring
on Faraday cups, the corrections (eqns. 11 and 16) can be simply added as functions to
static multi-collection ADS files set up in parallel with existing U metal files but
measuring masses 265, 267, and 270. For single collector Daly measurements, these
corrections can be done off-line (for example as a group of cells within the ‘Reduce Data’
page of Pb-MacDat).

These algorithms, including the assumed $^{18}\text{O}$ abundance were confirmed empirically at
MIT by splitting large spiked sample U loads and running as both metal and oxide. When
combined with the sample Pb isotope abundances, there was excellent agreement (better
than 0.1%) in calculated Pb/U ratios between the metal and corrected oxide uranium
isotope measurements.

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